Deglacial Si remobilisation from the deep-ocean reveals biogeochemical and physical controls on glacial atmospheric CO2 levels

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Abstract: During the last glacial period, the sluggish deep Ocean circulation sequestered CO2 into the abyss leading to the lowering of atmospheric CO2. The impacted of this redistribution on biologically essential nutrients remains poorly constrained. Using sedimentary □30Si of diatoms and biogenic accumulation rates in the Eastern Equatorial Pacific (EEP), we present evidences for the remobilisation of dissolved Silica (DSi) along with carbon from the deep ocean during the Last Deglaciation. Because DSi is essential for diatoms growing in the surface ocean, its concentration in the abyss during the glacial periods amounts to a negative feedback on the oceanic CO2 uptake. However, this effect can be muted by the increased Fe inputs during glacial periods which reduces diatom Si requirements in Fe limited regions such as the EEP. Our results from the EEP suggest that the efficiency of the biological CO2 pump and the size of the local CO2 source is tightly controlled by changes in DSi utilisation driven by Fe availability across the last glacial-interglacial transition.
We use a modified PANDORA box model to illustrate that the inventory of DSi in the global ocean surface is controlled by Fe availability in HNLC areas rather than by straightforward Si supply though upwelling. The Holocene is characterised by a fast mode of Si cycling driven by high biological requirement for Si under conditions of iron limitation and efficient overturning, promoting CO2 outgassing and an inefficient biological C pump via the rapid exhaustion of DSi in the surface. The last glacial period saw slower marine Si cycling as a result of decreased DSi biological requirement under Fe-replete conditions in the sea surface and increased Si and CO2 sequestration in the abyssal ocean. The switch between the two modes of Si cycling happened at 15ka BP, i.e. mid-deglaciation, and resulted in contrasting biological carbon drawdown responses in the EEP and globally between both phases of the deglacial CO2 rise. This illustrates that in addition to deep-sea CO2 storage and overturning, the efficiency of the biological pump also plays a crucial

role in determining ocean-atmosphere CO_2 exchange and shows the dual controls of ocean circulation and Fe-Si availability in this process.

Dear Prof. Robinson,

Please find our manuscript entitled **"Deglacial Si remobilisation from the deep-ocean reveals biogeochemical and physical controls on atmospheric CO2 levels"** by Pichevin L., Ganeshram R. and Dumont M.**,** which we submit for your kind consideration for publication.

Low atmospheric CO_2 concentration during the last glacial period compared to the Holocene are widely attributed to reduced ocean overturning which sequestered carbon in the abyssal ocean[1,2]. The last deglaciation saw the resumption of deep overturning, accompanied by surges of CO_2 outgassing, mainly via the Southern Ocean. While the paleoceanographic community has largely focussed on locating the origin and pathway of the carbon physically released to the atmosphere during the deglaciation[1], the impact of ocean stratification and the subsequent overturning events on the marine nutrient cycles and the marine biological carbon pump is largely unknown. Our manuscript addresses this crucial gap in knowledge.

Emerging evidences (Dumont el al., under review in Nature Communications) of global reorganisation in marine silica (DSi) distribution and partitioning during the deglaciation suggest that shifts in nutrient cycling, and silica in particular, could actively control PCO_2 via its effect on the marine carbon chemistry (organic vs. inorganic carbon export ratio) and the biological carbon pump[3]. The eastern Equatorial Pacific (EEP), today's greatest marine hotspot for CO_2 efflux to the atmosphere, is located at the receiving end of the Antarctic intermediate water nutrient conveyor and on the Southern Ocean degassing limb during the deglaciation. Therefore, the EEP represents an ideal setting to investigate the implications of the global changes in marine Si cycling for the biological C pump across the last glacial cycle, including the deglaciation.

We present biogenic export data and a zonal transect of 3 silicon isotope records from the EEP during the last 30 ka. Our new records confirm that the cycling of marine silica changed dramatically between glacial and interglacial epochs. The change in silicic acid cycling during the deglaciation matches closely the existing record of CO_2 sea-air exchange in the EEP (boron isotope records[4]) and provide the mechanism responsible for the increase in the deglacial CO_2 source from the EEP. We argue that Si utilisation changes driven by Fe availability determine the efficiency of the biological CO_2 pump in the EEP and control the size of the local CO_2 source. This illustrates that in addition to deep-sea CO_2 storage and overturning, the efficiency of the biological pump also plays a crucial role in determining ocean-atmosphere CO_2 exchange and shows the dual controls of ocean circulation and Fe-Si availability in this process.

The deglacial change in Si cycling and its implications on the biological pump are not restricted to the EEP or other high Nutrient Low Chlorophyll (HNLC) regions. Our modelling work suggests that the inventory of DSi in the global ocean surface is controlled by Fe availability in HNLC areas rather than by straightforward Si supply. On one hand, the Holocene is characterised by a fast mode of Si cycling driven by high biological requirement for Si under conditions of iron limitation and efficient overturning. This configuration promotes CO_2 outgassing and an inefficient biological C pump via the rapid exhaustion of DSi in the surface. On the other hand, the last glacial period saw slower marine Si cycling as a result of decreased DSi biological requirement under Fe-replete conditions in the sea surface and increased Si and CO_2 retention in the abyssal ocean. This configuration has the net effect of promoting CO_2 sequestration in the ocean and an efficient biological pump driven by high Fe and DSi inventory in the global sea surface. The switch between the two modes of Si cycling happened at 15ka BP, i.e. mid-deglaciation, and resulted in contrasting biological carbon drawdown responses in

the EEP and globally between both steps of the deglacial CO_2 rise. While the first event is mainly caused by physical remobilisation of marine CO_2, an inefficient biological C pump aided the second CO_2 rise.

The wider implication of our findings is that the interplay of the marine Si cycling feedbacks may have held atmospheric CO_2 concentrations to oscillate between remarkably consistent lower and upper limits during glacial-interglacial cycles throughout the Pleistocene.

We believe our new results have profound ramifications for understanding the causes atmospheric CO_2 changes and their relationship with past changes in nutrient cycling and circulation. Given these important implications, the report should interest a broad spectrum of EPSL readers.

Sincerely,

Dr. Laetitia Pichevin

Senior Researcher, University of Edinburgh

1 Rae, J. W. B. *et al.* CO 2 storage and release in the deep Southern Ocean on millennial to centennial timescales. *Nature* **562**, 569-573, doi:10.1038/s41586-018-0614-0 (2018).

2 Skinner, L. C., Fallon, S., Waelbroeck, C., Michel, E. & Barker, S. Ventilation of the Deep Southern Ocean and Deglacial CO(2) Rise. *Science* **328**, 1147-1151, doi:10.1126/science.1183627 (2010).

3 Archer, D. & Maier-reimer, E. Effect of Deep-Sea Sedimentary Calcite Preservation on Atmospheric Co2 Concentration. *Nature* **367**, 260-263 (1994).

4 Martinez-Boti, M. A. *et al.* Boron isotope evidence for oceanic carbon dioxide leakage during the last deglaciation. *Nature* **518**, 219-U154, doi:10.1038/nature14155 (2015).

***Revision Notes**

Dear Editor,

We are pleased to submit the revised version of our article entitled “Deglacial Si remobilisation from the deep-ocean reveals biogeochemical and physical controls on glacial atmospheric CO2 levels”.

We thank the Reviewer for their positive review of the manuscript highlighting the key points of the argument and for supporting its publication in EPSL.

We reply to the Reviewer’s comments (blue) in detail below (black) and have made the suggested changes in the text.

Reviewer #1: This is a highly synthetic paper containing some high quality records of Si isotopes from the Equatorial Pacific. These data are combined with Si isotope data from other proxies from the same cores, the modern water column of the equatorial Pacific and modeling to examine how silicon dynamics during the last glacial cycle may have modulated changes in atmospheric pCO2. The end result is an intriguing set of hypotheses that reconcile what has been an apparent contradiction between greater silica production in surface waters at times when Si supply would have been reduced due to sequestration of dissolved Si in deep waters. Key is the interplay between iron supply and diatom demand for silicon. There have been examinations of how interactions between silicon and iron dynamics may have influenced nutrient dynamics and atmospheric pCO2 during glacial cycles in the past, but this is the first effort to couple surface processes to dynamics in deep waters and it is done very sucessfully. The present work addresses directly how deep sequestration of CO2 and silicic acid in the deep ocean during glacial times can be reconciled with evidence for concurrent elevated diatom productivity and export in surface waters.

The data lead to the hypothesis that an inverse relationship existed between the timing of iron supply to surface waters via atmospheric dust and the reduction of the deep overturning circulation, which sequestered silicic acid and carbon in deep waters. Because diatom demand for Si relative to C increases under low Fe, the hypothesis is that during the Fe-rich slow-MOC glacial period the decrease in per capita Si demand by diatom cells could maintain high levels of productivity despite the lower Si supply imposed by Si sequestration in deep waters. Reinvigoration of the MOC during deglaciation lead to increased Si supply, but lower Fe inputs compensated through a decline in the Si:C content of diatoms creating a negative feedback on CO2 dynamics. These shifts in the efficiency of the biological pump may have modulated CO2 oscillations during glacial cycles.

The data set is of high quality and consistent with the hypotheses presented even in details. For example, the accumulation of isotopically light Si in deep waters during glacial times should produce a transient lightening of diatom Si isotopes upon reinvigoration of the MOC. Such a transient signal is observed in the Si isotope records. The conceptual framework assembled here is well worth publishing.

While I support publication, there are areas that can be improved.

General:

1) Throughout the paper the idea of a sluggish meridional overturning circulation leading to the sequestration of CO2 and nutrients (especially silicic acid) in deep water is presented as a given. While relevant citations are provided in key areas more detail would really justify both the conceptual arguments and model construction. The important issue is what is really meant by 'deep

ocean'. I believe the authors have it 'right', but a bit more detail on what is known about the changes in the ocean's 'upper' and lower' circulation limbs (i.e. like Toggweiler's red and blue circulations) would be useful. For example, NADW was replaced with Glacial North Atlantic Intermediate water which apparently was shallower such that the lower limb expanded in this basi[n]c. Key is to present the evidence that set the ocean divide (Fig 3) at 2500m splitting intermediate and abyssal circulation. The information is in the literature. A brief reiteration of the evidence would broaden the appeal of this paper. This might best be done in the supplemental material.

We thank the reviewer for this helpful comment and we agree that characterising what constituted the "deep ocean" during the glacial period and better describing the changes in global ocean circulation at that time will make the argument clearer and stronger. As the reviewer points out, the evidences already exist in the literature and we have briefly reiterated these in the text of the manuscript (lines 194-200). We cite new evidences based on both sponge and diatom δ^{30}Si records from the Southern Ocean (Dumont, accepted) which strongly support our hypothesis that DSi was sequestered in the deep ocean during the last glacial cycle and reinjected in the upper ocean during the deglaciation.

2) The dynamics id Si supply for the Equatorial Pacific are derived through teleconnections with the Southern Ocean. As the authors discuss the SO is another HNLC region so it should be subject to the same forcing as the equatorial Pacific, at least relative to Fe supply which increased in both regions during glacial periods. However, I do not see any examination of silicon isotope records from the SO to see if the predicted signatures are there. I did look at a few papers to see if the transient during the YD was there. It appears in a few records depending on how critically you trust the age models. A critical examination would prove if those records support the claims in this paper. The authors should include such an examination. If the signal is not there in the SO the hypothesis presented here is weakened.

Regarding the lack of examination of Si isotope records in the southern ocean, we believe the reviewer missed the reference we make to the existing Southern ocean records (line 283-286), one of which is shown in Figure 2B. These records provide new evidences for the sharp decrease in d30Si during the YD in the SO, the impact of which we witness in our EEP records. A newly published paper (Dumont et al., 2020 accepted in Nature communications) provides further evidence of the large scale, SO-wide decline in surface δ30Si at that time. We now make this observation and the connection between the SO and the EEP more explicit in the revised text (line 286, blue).

Specific:

Line 70-83: Mass spectrometry details. Currently details of reproducibility (precision) are given. It would be useful to report measured values for secondary standards like Big batch or Diatomite that have measured consensus values to illustrate accuracy as well.

This has been added to the method section (lines 81-84).

Line 338: Change "deglaciation should brought" to "deglaciation should have brought"

This has been corrected.

Figure 3 confused me until I read the supplemental materials. The boxes on the right are easy to mistake for the PANDORA model itself based on the text. I was initially confused as the arrangement of the boxes look like the CYCLOPS model as there are too few boxed for it to be the PANDORA model. If the figure caption explained that these were the output for the Pacific sector of the PANDORA model it would be helpful. Also the model results in Fig3A are mislabelled as there are no Pacific Surface data shown. What is in the upper box is the result for Pacific Intermediate. Adding the Surface Pacific would be useful. Also check the data in Fig 3 against the PANDORA results in the supplemental materials. There are inconsistencies. For instant in the supplement the SO interior during the Holocene has a DSI concentration of 84 while a value of 81 is shown in Fig 3c for this water mass.

We thank the reviewer for highlighting the inconsistency in DSi concentration between both figures to us. We have now corrected accordingly in figure 3 and point out that only Pacific boxes are shown in the figure caption (line 424) and in the text (lines 204-205, blue).

The concentration and isotopic signal of DSi in the Pacific Surface box is presented in the supplementary material. The concentration in this comparatively small water mass is very low (2µM and 0.5/0.6 µM during the Holocene and the LGM, respectively) and therefore represents a very small component of the global Pacific Si inventory at both times. The Surface pacific δ^{30}Si is also not straightforwardly representative of the isotopic signal recorded in the diatoms because the latter is subject to further fractionation via relative utilisation, which as we point out in lines 219-221, changed between the Holocene and the LGM. We do not represent the concentration and isotopic signal of the surface small box in Figure 3 to avoid confusion, but the information is presented in the supplementary material.

Reference

Dumont, M.D., et al., *The nature of deep overturning and reconfigurations of the silicon cycle across the last deglaciation* Nature Communications, 2020. **Accepted/in press**.

Highlights

- Glacial Si sequestration in the Deep Ocean moderated by Fe availability
- Deglacial remobilisation of dissolved Silica from the deep Ocean
- Fe-driven Si utilisation changes determine the size of the CO_2 source in the Eastern Equatorial Pacific
- Dual controls of ocean circulation and Fe-Si availability on global ocean-atmosphere CO_2 exchange

Deglacial Si remobilisation from the deep-ocean reveals biogeochemical and physical controls on glacial atmospheric CO_2 levels

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Abstract- During the last glacial period, the sluggish deep Ocean circulation sequestered CO_2 into the abyss leading to the lowering of atmospheric CO_2. The impacted of this redistribution on biologically essential nutrients remains poorly constrained. Using sedimentary δ^{30}Si of diatoms and biogenic accumulation rates in the Eastern Equatorial Pacific (EEP), we present evidences for the remobilisation of dissolved Silica (DSi) along with carbon from the deep ocean during the Last Deglaciation. Because DSi is essential for diatoms growing in the surface ocean, its concentration in the abyss during the glacial periods amounts to a negative feedback on the oceanic CO_2 uptake. However, this effect can be muted by the increased Fe inputs during glacial periods which reduces diatom Si requirements in Fe limited regions such as the EEP. Our results from the EEP suggest that the efficiency of the biological CO_2 pump and the size of the local CO_2 source is tightly controlled by changes in DSi utilisation driven by Fe availability across the last glacial-interglacial transition.

We use a modified PANDORA box model to illustrate that the inventory of DSi in the global ocean surface is controlled by Fe availability in HNLC areas rather than by straightforward Si supply though upwelling. The Holocene is characterised by a fast mode of Si cycling driven by high biological requirement for Si under conditions of iron limitation and efficient overturning, promoting CO_2 outgassing and an inefficient biological C pump via the rapid exhaustion of DSi in the surface. The last glacial period saw slower marine Si cycling as a result of decreased DSi biological requirement under Fe-replete conditions in the sea surface and increased Si and CO_2 sequestration in the abyssal ocean. The switch between the two modes of Si cycling happened at 15ka BP, i.e. mid-deglaciation, and resulted in contrasting biological carbon drawdown responses in the EEP and globally between both phases of the deglacial CO_2 rise. This illustrates that in addition to deep-sea CO_2 storage and overturning, the efficiency of the biological pump also plays a crucial role in determining ocean-atmosphere CO_2 exchange and shows the dual controls of ocean circulation and Fe-Si availability in this process.

Keywords : Marine Silicon cycle, Last Deglaciation, marine CO_2 source, Eastern Equatorial Pacific

Introduction

Strong stratification of the deep ocean is invoked to explain the lowering of atmospheric CO2 levels during the glacial periods. Such isolation of the deep ocean trapped more of the respired carbon and nutrients in the abyss reducing their availability to biota and atmospheric exchange at the surface [1-3]. Dissolved silicic acid (DSi), a nutrient essential for diatom growth, is particularly sensitive to such strong segregation due to the deep regeneration of sinking biogenic silica in the ocean relative to other soft tissues nutrients (C,P and N) [4]. As a result, the upper ocean during glacial periods should have been progressively stripped of silicic acid at a greater rate than nitrate and phosphate, limiting its availability while the stratified deep ocean should have become increasingly enriched with DSi. The consequent decrease in siliceous phytoplankton production, relative to calacerous, should have reduced the efficiency of the biological pump by lower organic to carbonate C rain rate ratio [5]). This should have offset the lowering of atmospheric CO2 resulting from carbon sequestration in the glacial deep ocean [6]. However, palaeoceanographic records paint a different picture [7-11]. Broadly, diatom-bound silicon isotopic signal (δ^{30}Si) and/or biosilica export in the Southern Ocean (SO), Atlantic, tropical Pacific and Subantarctic [7-11] indicate greater DSi availability and/or diatom production during the LGM relative to the Holocene. How can we reconcile the increased deep DSi sequestration produced by the isolation of the deep ocean and greater Si availability in the surface ocean? Addressing this issue is crucial to fully account for the glacial lowering of atmospheric CO_2, and to understand the counteracting effects of ocean circulation and the biological pump in this process.

1- Material and Methods

We present diatom-bound silicon isotopes records and paleoproductivity reconstructions from 4 sediment cores distributed on a zonal transect in the EEP (ODP 1240, ODP 846, VNTR01-8PC and PC72; Figure 1) over the last glacial cycle in order to explore glacial-interglacial change in nutrient distribution and DSi availability in the EEP. The data are interpreted using modern δ^{30}Si and δ^{15}N from sea water and core tops from the area [12-14].

The sedimentary cores used (table S1) have established and published age models based on foraminiferal $\delta^{18}O$ records and/or AMS^{14}C dates on planktonic foraminifers, as well as biogenic silica and organic carbon fluxes and nitrogen isotope data [10, 15-20].

Purification of the diatom samples for silicon isotope measurement in Core ODP-1240, ODP 846, VNTR01-8PC and PC72, has been performed following published cleaning methods [21]. Silicon isotope determination has been conducted in ETH Zürich and at the Brian Price laboratory at the University of Edinburgh. A small amount of biogenic opal (0.2-0.5 mg) was dried down with concentrated perchloric acid at ~180°C in Teflon© vials, and then dissolved in 100 µl of 1 M NaOH, before being diluted to 5 ml with 0.01 M HCl after 24 hours. Equivalent to 10 µg of opal was loaded onto a pre-cleaned 1.8ml DOWEX 50W-X12 cation exchange resin bed (in H^+ form) and eluted with 5 ml of purified water (Milli-Q element 18.2 $M\Omega.cm^{-1}$). The Si isotope composition was determined on the diluted solution (0.6ppm Si) by MC-ICPMS, using a standard-sample-standard bracketing protocol. All results in this study were calculated using the $\delta^{30}Si$ notation for deviations of the measured $^{30}Si/^{28}Si$ from the international Si standard NBS28 in parts per thousand (‰). The long-term reproducibility was calculated using measurements of Big Batch standards over the period of analyses and found to be better than 0.14‰ for $\delta^{30}Si$ (2 s.d.) [22]. The Big Batch standard $\delta^{29}Si$ and $\delta^{30}Si$ gave values of -5.39 +/-0.05‰ and -10.56+/-0.1‰, respectively (to be compared with published values of −5.35‰ and −10.48‰ [23]). Samples were measured at least 2-4 times, which resulted in a 95 % confidence level below 0.08‰.

To conceptually investigate the impact of deep ocean stratification on DSi distribution and partitioning during glacial time, we adapted the PANDORA model (Sup. Mat. 3) by adding an abyssal box that can be isolated from the rest of the ocean circulation [24-26]. The box model setup is similar to the PANDORA architecture of Peng et al (1993) and Reynolds (2009). The major change is the inclusion of an abyssal Southern Ocean/Pacific box so that isolation of deep waters can be simulated. The water fluxes between boxes for the control (Holocene) setup have been taken from Peng et al (1993), with the Southern Ocean outputs re-routed through the Abyssal box (Figure S5).

2- Results and interpretations

2.1- Glacial-interglacial variability in Si utilisation in the EEP

The modern EEP is an important region of CO_2 efflux from the ocean (Figure 1A) due to the upwelling of the Equatorial Undercurrent (EUC) and its status as an Fe limited High Nitrate Low Chlorophyl (HNLC) region [27-29] (Figure 1A). We reconstruct the East-West gradient

in silicic acid utilisation in the EEP for modern and glacial periods (Figure 1B). Modern estimates are calculated from the difference between surface and initial subsurface (EUC core, 100-150 m water depth) DSi concentrations as well as published δ^{30}Si of DSi [13, 14]. Isotopic discrimination following Rayleigh fractionationation kinetics during biological uptake, results in lighter δ^{30}Si composition of biogenic silica relative to DSi substrate. Therefore the presence of unutilised DSi left in the surface ocean results in lighter sinking biogenic Si. We exploit this to reconstruct Si relative utlisation from diatom remains in coretop (modern) and glacial sediments. (Sup. Mat.1, table 1). The similarity in the zonal trends of watercolumn and core top sediments based Si utilisation validates the suitablity of the isotopic approach for our glacial reconstructions.

Modern surface DSi concentration in the EEP is low, at about 8 µmole/L at the equatorial divergence where the EUC upwells and, within a few degrees North and South of the Equatorial divergence, decreases rapidly to <4 µmole/L [14]. At such low levels of Si(OH)4 (<4 µmole/L) diatoms experience kinetic limitation during growth, their metabolism slows down and they become outcompeted by other phytoplankton groups [14]. The calculated DSi relative utilisation is high and surprisingly constant across the EEP, ranging from 65% in the eastern most part of the EEP where upwelling rates are greatest to 80% between 90 and 140°W (Figure 1B). This high and rapid consumption of silicic acid in the modern EEP is also confirmed by existing Si isotope measurements on dissolved Silica [13]. DSi is rapidly and extensively utilised after reaching the surface in the divergence, curtailing its spatial spread westward and poleward and resulting in an apparent flat gradient between 86 and 140°W. In contrast, nitrate relative utilisation increases progressively westwards [12, 20] and the zonal gradient denotes a more gradual consumption relative to that of $Si(OH)_4$ (Sup. Mat 1, Fig.1B). The difference between the DSi and NO_3 zonal utilisation gradient results from the greater, more rapid consumption of DSi compared to nitrate in the sea surface and is only possible if the biota Si:N uptake ratio exceeds 1. Considering that both calcareous and siliceous phytopklancton bloom in the EEP and use nitrate (Si is only used by the latter), the diatom specific Si:N uptake ratio must be even larger (>1) than the community uptake ratio, indicating iron limitation[30]. This discrepancy is indeed largest in the easternmost part of the basin where dissolved iron concentration in the mixed layer are vanishingly low < 0.1 nmol.L. i.e., below biological requirements (Fig. 1B) [31, 32]. Given that Si:N uptake ratio of diatoms growing under Fe stress is up to 4 and much higer than diatom growth under normal conditions (~1;[30]), this confirms that Fe limitation in the modern EEP is responsible for the excessive consumption of silicic acid relative to nitrate. This drives the depletion of Silicic

136 acid to levels below kinetic limitation for diatoms, while leaving excess nitrate in the surface
137 similar to other High Nitrate Low Chlorophyll (HNLC) regions such as the SO.
138
139 The East-West difference (gradient) in silicic acid utilisation over the last glacial cycle was
140 reconstructed using 4 sediment cores (Fig. 1 and Sup. Mat. 1) [33]. Silicic acid relative
141 utilisation during the LGM was lower in the EEP and the zonal gradient shows a more
142 progressive DSi utilisation trend than today, resulting from a greater east-west difference in
143 relative utilisation. Glacial utlisation is 45% in the eastern most part comapred to today
144 (65%) (Fig.1B). We attribute these features as diagnostic traits of relatively Fe replete
145 conditions during the LGM indicating that the EEP was not a HNLC region at that time [10,
146 34, 35]. As a result substantial silicic acid availability was maintained in the sea surface of
147 the EEP and unused DSi could be dispersed away from the upwelling centre [10].
148
149 **2.2- Deglacial switch in HNLC status of the EEP**
150
151 The timing of the switch in nutrient status across the last glacial Termination can reveal
152 important clues into the factors responsible. We use three cores with well resolved deglacial
153 sequences forming a zonal gradient across the EEP to reconstruct past changes in the
154 nutrient status (HNLC conditions) of the EEP (Fig. 2c). The Zonal gradient (Fig. 2h) is
155 calculated as the difference between the δ^{30}Si signal measured in the western-most core
156 (VNTR1-8PC) and that of the eastern-most core (ODP12-40) at any given time-period. The
157 δ^{30}Si records from these cores show a large zonal gradient during the LGM (0.6-1‰; Fig. 2h)
158 suggesting the spatial spread of relatively unutilised Si characteristic of the Fe-replete
159 condition. This situation persisted during the first half of the deglaciation. The gradient
160 collapses and the values converge after 15Ka to reach its lowest values (<0.2‰) during the
161 Younger Dryas (YD) and the beginning of the Holocene (Figure 2h). This timing is in phase
162 with the reduction in dust-borne Fe supply to the region during the last glacial termination,
163 confirming the role of Fe in influencing Si utilisation (Fig. 2a)[36]. Greater wind-born Fe
164 supply globally and to the EEP during the glacial periods should reduce silicic acid
165 overconsumption during diatom growth by removing Fe limitation and increase the avialablity
166 of DSi [10]. We argue that during the deglaciation (at about 15 ka), the nutrient status of the
167 EEP switched to Fe limited HNLC regime, leading to increased Silicic acid consumption
168 responding to the reduced dust-borne Fe supply.
169
170 The global increase in dustiness by several fold provided an additional Fe supply during the
171 LGM [34]; As a result the demand for silicic acid by diatoms in the EEP and other modern

HLNC regions should have decreased to lower Si:N uptake ratio by diatoms. For instance. silicon isotope records from the Antarctic zone of the southern ocean [8] (Fig. 2b) also confirms greater Si availability (lighter δ^{30}Si) during the LGM compared to modern HNLC condition of near complete Si consumption [37]. The generation of unutilised excess DSi in HNLC regions such as the EEP and SO should have in general increased the availability of silicic acid promoting marine diatom production outside of these areas through dispersion during glacial periods. For instance, the excess DSi generated in the SO could be dispersed through mode and intermediate waters increasing diatoms production in low latitudes [38]. This is in agreement with existing records showing greater Si availability and biosilica accumulation in the Atlantic, Pacific and Subarctic basin during the glacial period despite deep ocean stratification and the proposed sequestration of DSi in the ocean abyss [7-11]. The implication of this finding is that surface Ocean Si avalability is controlled by Fe status rather than global upper ocean DSi inventory. At 15Ka BP the global marine Si cycle switched from glacial conditions of low Si biological demand in the ocean's surface, reduced Si turnover in the deep ocean and biological production largely limited by N or P[10] to more rapid DSi turn over in deep ocean and more complete consumption of DSi by diatoms under conditions of Fe Si co-limitation. This allows us to reconcile the greater glacial availability of DSi in many part of the surface ocean despite deep ocean DSi sequestration during glacial periods. Below, we explore this shift in marine Si cycling on the of DSi distriution in the ocean and the partitioning of Si isotope signature in the ocean using a box model.

3- Discussion

3.1- Partitioning of Si in the Glacial Ocean

Today, the deep and upper water masses upwell and mix in the SO and are redistributed to the rest of the ocean basins. Compared to today, the global ocean circulation was dramatically different during the LGM. LGM models and proxy reconstructions reveal that sea ice cover and the northward shift in the Westerlies isolated deeper water masses preventing mixing with the upper overturning cell (figure 3) [39, 40]. In such circumstances, nutrients, and in particular silicic acid become trapped in the isolated deep water masses, below 2500 m water depth [37].

We use a box model to conceptually investigate the impact of slow and fast Si cycling as well as changes in Fe limitation on the DSi distribution and isotopic composition. We adapted the PANDORA model by adding an abyssal box that can be isolated from the rest of the ocean circulation [24]. The results are presented in Figure 3 for the Pacific and SO basins and in the Supplementary Material for the whole ocean. The LGM scenario presented is not intended to be a quantitative reconstruction but rather a demonstration of how the proposed glacial-interglacial change in the Si cycle impacts the distribution of DSi inventory

and silicon isotopes. In the model the physical isolation of the deep ocean during the LGM [1] leads to the accumulation of DSi in the abyss and a progressive reduction in DSi inventory in the rest of the ocean. However, reducing the relative uptake of DSi in the SO surface during the glacial period due to Fe fertilization allows DSi to be advected to the low latitude through glacial Antarctic Intermediate water circulation, hence increasing its availability in the global sea surface. This is despite the enhanced accumulation of DSi in the deep glacial Ocean. The terrestrial DSi source to the ocean was kept unchanged relative to modern in these simulations. However, there are evidences that the whole DSi inventory to the ocean was slightly greater during the LGM [37], which would have amplified both the increase in DSi concentration in the abyss and DSi availability in the surface ocean.

Due to isotopic fractionation during biological uptake, biogenic silica has a lighter $\delta^{30}Si$ composition than the DSi substrate and the unutilised DSi left in the surface ocean is likely considerably heavier than the sinking Si. The global $\delta^{30}Si$ signature of the deep ocean DSi is strongly influenced by the biogenic Si sink in the SO [41]. In the present mode of Si cycling (DSi overconsumption in HNLC regions), almost all of the silicon is biologically used and exported below the mixed layer and either recirculated upon regeneration or exported to depth, resulting in a small surface DSi pool. This results in very small isotopic partitioning within the surface and well-mixed ocean interior (Fig. 3) [41]. In contrast, the slow Si cycle during the LGM consisting of lower relative utilisation of DSi in the surface ocean would amplify the isotopic partitioning of DSi between surface, intermediate and deep ocean, leading to comparatively higher DSi concentration and lighter $\delta^{30}Si_{diss}$ in the isolated glacial ocean abyss (regenerated Si) relative to the intermediate depth Si pool (partially utilised, preformed Si).

The lower and intermediate circulation limbs were separated during the LGM, allowing isotopic segregation between an accumulating stock of regenerated Si (light) in the abyss and a lessening stock of preformed DSi (heavy) in the upper and intermediate circulation branch [42]. However, this heavy source of DSi supplied to the surface is not fully expressed in biogenic silica produced at the sea surface where Fe replete conditions prevented complete Si utilisation and maintained relatively light $\delta^{30}Si$ composition of biogenic silica detritus settling to the sediments from the surface (fig. 2b &c) and maintaining the isotopic fractionation between the regenerated and preformed Si pools (Fig. 3). The resumption of the overturning circulation during the deglaciation is expected to result in the deglacial flushing of the regenerated light Si pool through the SO bringing light Si isotopic signature to the surface of the SO and through intermediate waters to the low latitudes. At the same time, the merging between the lower and upper limb of the ocean circulation [43] caused the

mixing of both regenerated and performed DSi pools and the progressive disappearance of the isotopic partitionning.

It is worth noting that a δ^{30}Si record from the North Pacific shows a moderate increase during the Deglaciation [11]. We attribute this slightly heavier δ^{30}Si to the flushing of the heavy preformed Si pool through the North Pacific at a time of invigorated vertical mixing in the subarctic Pacific [44], in agreement with our conceptual model which simulates a slight increase in intermediate depth, preformed δ^{30}Si in the glacial North Pacific (Fig. 3). The box model demonstrates that the sequestration of DSi in isolated abyssal waters decreases the inventory of DSi in upper ocean (intermediate and surface ocean); however, the impact of reduced DSi inventory in the surface ocean is mitigated by the lower Si:N uptake ratio of diatoms in modern HNLC regions such as the SO and EEP. This keeps DSi avaibility high at the surface in the glacial ocean. One important result of the model is the isotopic partitioning between the abyss and the upper ocean during the glacial. Considering that the SO and the associated intermediate water is identified as an important pathway for deep water upwelling and its advection to low latitudes,the flushing and mixing of the isotopically light glacial DSi pool from the abyss into the upper ocean during the deglaciation should leave a mark in deglacial age sediment in the EEP.

3.2- Evidence for deglacial shift in global Si cycling.

The remobilisation of isolated deep ocean waters with higher Si concentrations and light δ^{30}Si signatures at the end of last glacial period should leave a transient signature in palaeoceanographic records during the deglaciation. Here we show paleoceanographic evidences of this in the EEP. Thorium normalised biogenic silica (and organic carbon) export fluxes recorded in multiple sites in the EEP (Figure 1A) increased by 1.5 to 3 folds during the deglaciation (Figure 2d, e), indicating that biological productivity and export peaked at that time relative to the LGM and the Holocene. Such high biological fluxes can only be achieved by the supply of additional nutrients, and in particular, silicate in the sea surface, in response to either (1) enhanced nutrient concentration in the EEP thermocline waters or (2) invigorated upwelling in the equatorial divergence. Evidences based on stable and radiogenic carbon isotopes suggest that the deglacial productivity peak was caused mainly by channelling nutrient-rich waters from the SO through the Equatorial Under Current (EUC) system to the EEP (sup. Mat. 2) rather than increasing equatorial upwelling rate [17] [33]. This supports the nutrient tunnelling hypothesis [45, 46] whereby the resumption of deep overturning at the end of the last glacial period in the SO created a pathway for the deep

ocean waters enriched in nutrient to reach the upper ocean circulation and fuel biological productivity in the lower latitudes in both the Pacific and the Atlantic Oceans, via the nutrient rich Antarctic Intermediate Waters (AAIW) [45, 46].

In the SO, the deglacial flushing of the deep DSi glacial pool appears to have occurred during the second warming events when the connection between the deep Pacific basin and the upper ocean circulation resumed, bringing isotopically light DSi (by up to 0.7 ‰ relative to today) to the surface as evidenced by the SO record shown in figure 2b [37]). We observe the imprint of this isotopically light Antarctic Si in our multiple δ^{30}Si records from the EEP during the YD (Fig. 2C). Crude estimates based on deep-sea sponge Si isotope and biogenic silica accumulation records from the subtropical Atlantic suggest that the supply of Silicic acid to the low latitudes increased by around 30-60% due to increased Si export from the Antarctic zone, via the AAIW, during the younger Dryas (Sup. Mat. 1, [46, 47]). This agrees well with the 50% increase in bioSilica export we observe in the EEP at that time, compared to the LGM and the Holocene (Fig. 2d&e). This supports the greatly enhanced Si supply from the SO and implies substantial relative utilisation of the available silica compared to other nutrients (Fig. 2). Taking into account both the SO and North Pacific sources of Si [48], we estimate the isotopic composition of the DSi supplied to the EEP surface to be 0.2+/- 0.04 ‰ lighter than today during the YD (Sup. Mat. 1). Using a Rayleigh fractionation model [49], we calculated that Si utilisation in the easternmost part of the EEP during the YD was at minimum 68+/-1.5%, similar to the holocene value (65%) but significantly higher than during the LGM (45%), corroborrating our findings that Si overconsumption triggered by Fe limitation in the easternmost part of the EEP was established during the YD (Sup. Mat. 1) and supported high Biosilica and Si:Corg export fluxes in the EEP at that time (Fig. 2 e&f). Thus deglacial light δ^{30}Si values in the EEP provide evidence for the segregation of the Si pool by recording the transient signal of its remobilisation during the deglacial deep ocean during glacial times. In addition it provides important insights into the operation of global Si cycle on glacial interglacial time scales.

The paleoceanographic records assembled from the EEP provide evidence for two key aspects of the glacial-interglacial change in Si cycle described in figure 3 (box model): (1) the transient relocation of deep ocean Si pool with lighter Si source from the Southern ocean marking the switch from slower to faster Si cycle particularly around the YD as predicted by the box model; (2) the surface ocean conditions and the switch to HNLC status during the deglaciation (~15Ka) responding to the decline in dust borne Fe supply and transition from glacial lower Si utilisation to more complete Si consumption by diatoms. During the glacial

period, the lifting of Fe limitation has two important effects. Locally within the HNLC regions such as the EEP and SO, it relieved Fe-Si co-limitation by reducing Si:N uptake of diatoms generating excess DSi and more globally,by making the excess Si available for diatom growth outside the HNLC regions. This is recorded in paleoceanographic records showing higher Si availbility and biogenic silica accumulation. Both of these processes have the net result of increasing the effciency of the biological CO_2 pump by increasing the C rain rate ratio of export production in the glacial ocean.

3.3- Implication for the marine C pump and atmospheric CO_2

The Equatorial Pacific, one of the largest oceanic sources of carbon dioxide, contributes to up to 2/3 of the marine CO_2 release to the atmosphere today [27, 28] (Figure 1). The strength of the CO_2 source in the EEP is set by the net effect of counteracting physical (upwelling) and biological (biogenic production) processes [27]. In the modern EEP, biological productivity and the associated fixation of carbon does not efficiently compensate for the physical outgassing of CO_2 due to its HNLC conditions and Fe limitation. Our results suggest that the switch to this HNLC status occurred around 15ka in response to declining to Fe inputs at the end of the glacial period when deep ocean circulation is undergoing a reinvigoration in the SO (Figure 2). Importantly, the EEP is part of the degassing limb of this ventilation process.

Boron isotope records have been used to reconstruct shifts in DIC/pH in EEP waters and to quantify the local CO_2 source to the atmosphere from the LGM to the late Holocene (Fig. 2g) [50]. The B record shows that the EEP was a net CO_2 sink during the LGM and switched to a net source during the Holocene. Our Si gradient proxy for HNLC conditions matches the boron isotope records closely (Fig. 2 h&g) where the EEP was a source of CO_2 to the atmosphere during the Holocene when HNLC condition was prevalent with DSi depletion across the entire EEP (flat zonal Si utilisation gradient) compared to the LGM. In contrast, during the LGM, the EEP was a net sink when HNLC conditions were lifted leading to greater relative availability of DSi at the surface, a larger δ^{30}Si zonal gradient and an increased organic carbon export (Fig.2).

The resumption of ocean overturning and the remobilisation of the isolated carbon pool during the deglacial should have brought CO_2 rich waters to the EEP through intermediate waters sourced in the SO. Boron isotopes record show that this peak in pCO_2 occurred during the YD but the source was subdued before 15 Ka during the early deglacial. This contrasting early and late deglacial CO_2 response is also matched closely by the δ^{30}Si zonal gradient, a marker for the efficiency of the biological C pump and HNLC status in the EEP.

This suggests that despite the invigorated deep ocean circulation and associated remobilization of carbon during the deglaciation (18-10 ka), the extent of CO_2 degassing depended on the efficiency of the biological pump. In the EEP the biological C pump was more efficient during the early deglacial partly compensating for the enhanced overturning and outgassing of CO_2. However during the late deglacial, and particularly during the YD, the establishment of HNLC status and the resulting inefficient biological pump lead to enhanced CO_2 outgassing. This illustrates that in addition to deep-sea CO_2 storage, the efficiency of the biological pump also plays a crucial role in determining ocean atmosphere CO_2 efflux and the dual controls of ocean circulation and Fe inputs in this process.

Conclusion

Our results suggests the operation of both positive and negative feedbacks in atmospheric CO_2 regulation on glacial-interglacial time scales involving ocean circulation and marine carbon, silica and Fe cycles. The sequestration of carbon in the sluggish deep ocean lowers atmospheric CO_2 levels during cold climate phases. Fe regulates the efficiency of the biological pump by changing diatoms requirement for DSi during growth in HNLC regions. Enhanced Fe availability during glacial stages increases the efficiency of the biological pump and, specifically, the carbon rain rate ratio of the exported primary production by keeping DSi available and promoting siliceous production in the HNLCs and low latitude sea surface, further sequestering CO_2. These two processes worked in tandem to lower atmospheric CO_2 levels during glacial times. While the reinvigoration of deep ocean circulation injected CO_2 back into the atmosphere during deglaciation, the atmospheric CO_2 level were maintained at a high level by an inefficient biological pump constrained by Fe and Si co-limitation in HNLC regions along with the absence of a deep, isolated C reservoir during interglacial times.

Our study reveals that Si cycling, however, also provides a negative feedback on CO_2 sequestration and release from the ocean by changing the upper ocean Si inventory. Sluggish glacial ocean circulation sequesters Si along with C into the deep ocean and depletes the upper ocean of DSi as evident in the box model. This potentially caps the biological uptake of CO_2 into the ocean. Conversely, when the deep ocean Si pool was mixed into the upper ocean along with carbon this additional Si supply serves to limit CO_2 outgassing and this cap is maintained during the interglacial periods by higher Si inventory in the upper ocean. The interplay of these positive and negative feedbacks collectively may have held atmospheric CO_2 concentrations to oscillate between remarkably consistent lower and upper limits during glacial and interglacial cycles throughout the Pleistocene.

Figure captions

Figure 1: (A) Map of modern sea-atmosphere Δ*PCO2* (µatm) showing the eastern equatorial pacicif (EEP) CO2 source hot spot. Stars mark the core locations (ODP 1240, ODP 846, VNTR01-8PC and PC72) and the box shows the area where the 6 sedimentary archives used to build the export production stack records were retrieved. (B) Silicic acid relative utilisation reconstructed from sea water samples (black circle) and core tops (solid black line, modern time) and glacial age sediment (doted lines) compared with Nitrate relative utilisation from sea water samples (red squares[12]) and sediment core tops (red line, modern) and with dissolved Fe concentration in the mixed layer (black cross) [31, 32]. The relative utilisation is calculated using the Rayleigh fractionationation model from N and Si isotopic signals obtained in both core top and sea-surface water samples. Both data sets are in good agreement (see Sup. Mat.).

Figure 2: (a) Th232 based dust input from core PC72 (black [34]) and ODP1240 (grey); (b) Silicon isotope records from cores MD-773 (Dumont et al, 2020[37]) in the Antarctic; (c) Silicon isotope records from cores ODP 1240 (red), ODP 846 (blue) and VNTR01-8PC (black); Stack records and standard deviation lines (dashed grey lines) of 230Th normalised organic carbon (solid grey, d), biogenic opal (green, e) and Si to Organic carbon accumulation ratio (red, f) in the EEP (core location in table, Sup. Mat. 2); (g) Boron isotope based reconstruction of Sea-air CO2 efflux in the EEP (black dots[50]); and (h) zonal gradients of d30Si (solid purple) and Si relative utilisation (dashed purple, %). YD stands for Younger Dryas, HS1 for Heinrich stadial 1 and ACR for Antarctic Cold Reversal.

Figure 3: Conceptual model of LGM to Holocene change in Si cycling (left) and the PANDORA simulation of the Pacific and Southern Ocean (SO) for the Last Glacial maximum (LGM) and the Modern (right). **A- LGM:** The lower and intermediate circulation limbs were separated allowing isotopic segregation between an accumulating stock of regenerated Si (light) at depth and lessening stock of preformed Si (heavy) in the upper circulation branch while Fe replete conditions at the sea surface prevented complete Si utilisation, maintained relatively light δ^{30}Si in the surface and isotopic fractionation between the regenerated and preformed Si pools. **B- Younger Dryas (YD):** The deglacial flushing of the regenerated, isotopically light Si pool through the SO after 15 Ka resulted in light Si isotopic signature recorded in the surface of the SO and EEP, whilst the merging between the lower and upper limbs of the ocean circulation [43] caused the mixing of the 2 Si pools and the progressive disappearance of the isotopic partitionning. The lower dust inputs caused Fe limitation leading to the establishment of HNLC status in the EEP **C- Holocene:** DSi overconsumption in HNLC region, Si is exported below the mixed layer and either recirculated or exported at depth, resulting in moderate isotopic partitioning between the surface and the well-mixed

ocean interior. The PANDORA box model results illustrate the potential associated changes in DSi concentration (blue, $\mu M.L^{-1}$) and isotopic signature (red, ‰) in Pacific water masses between the LGM and modern conditions. Only the model results for the Pacific and SO are shown (for full model results see Sup. Mat. 3).

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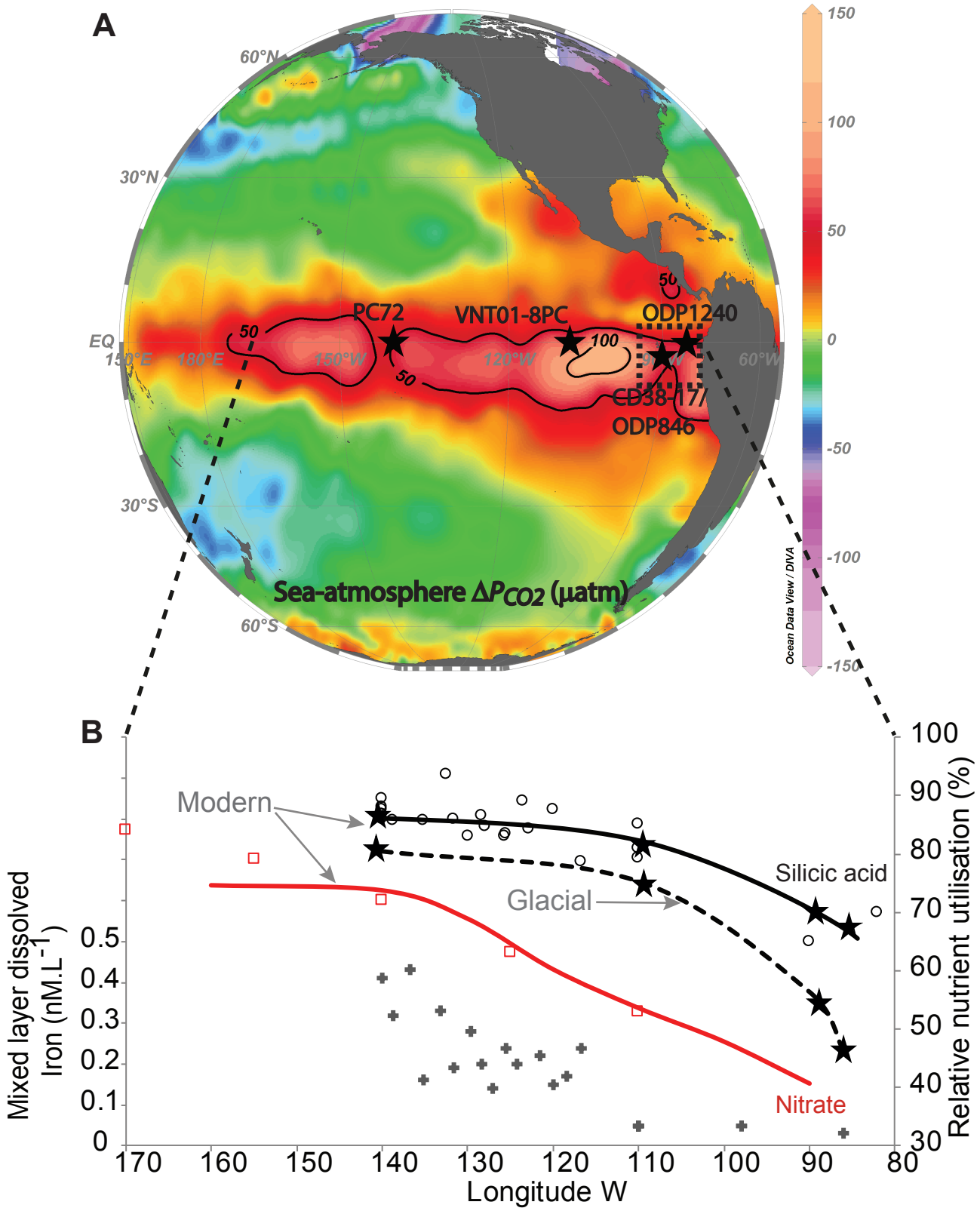

Figure 2

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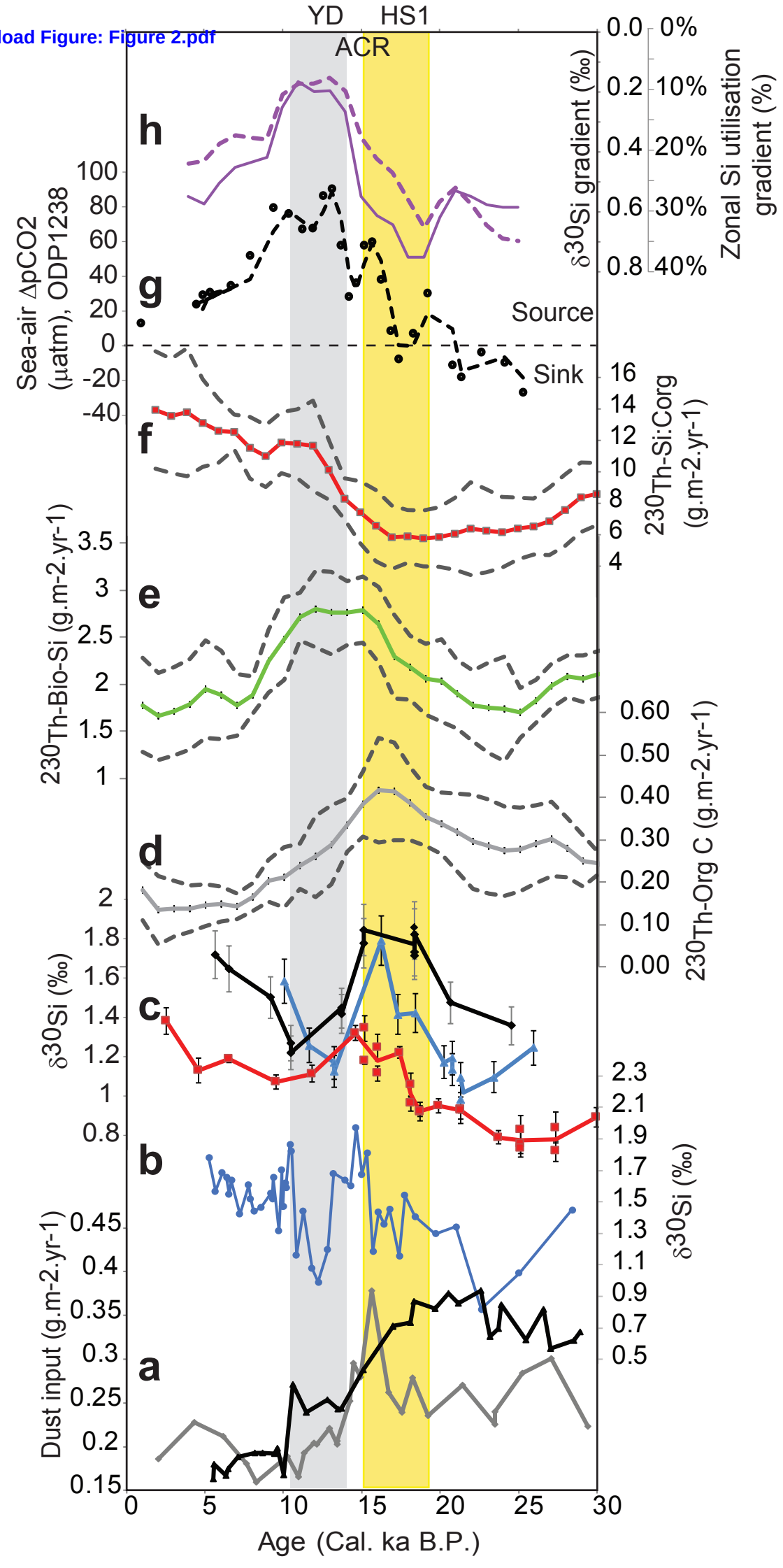

Figure 3

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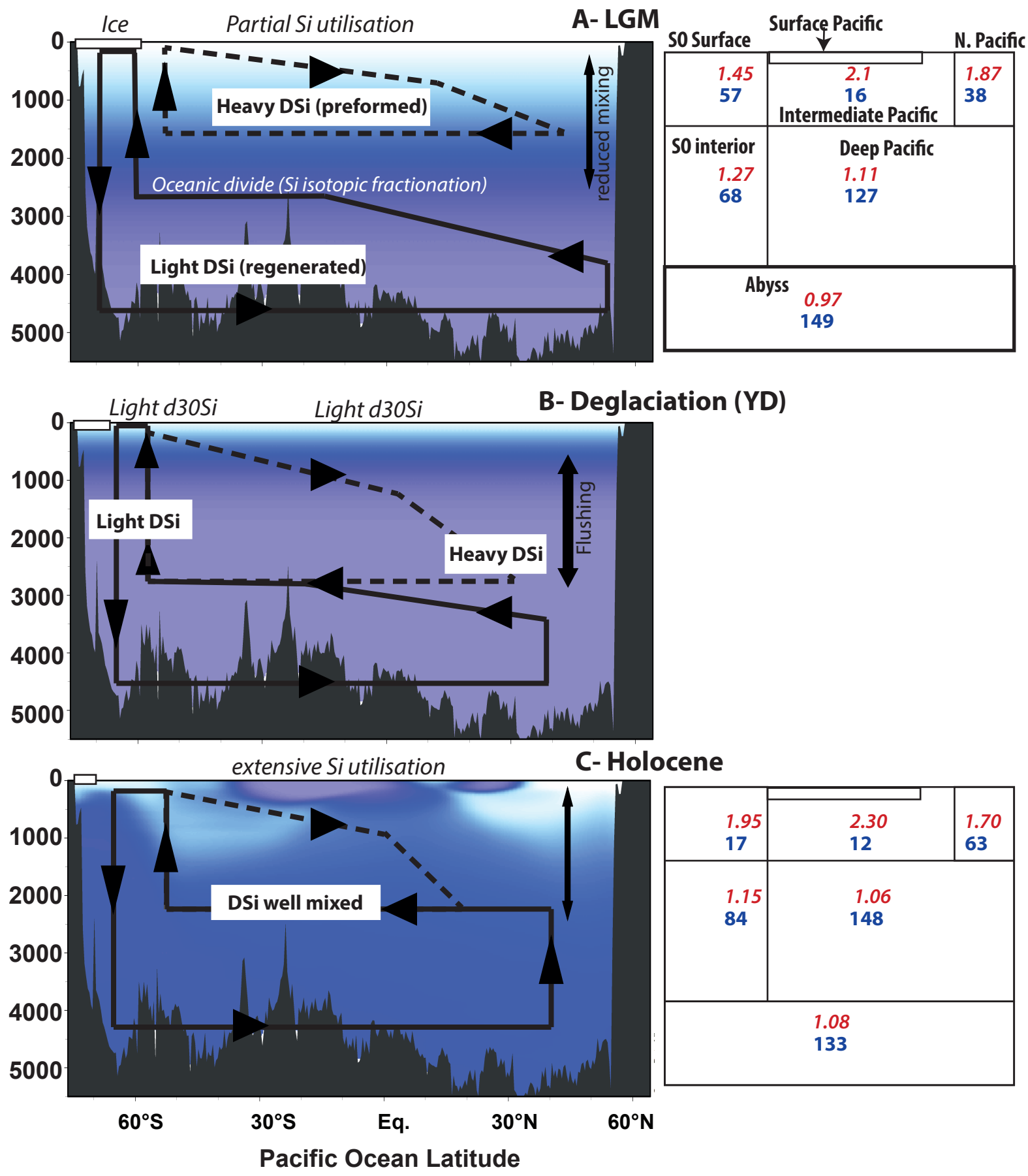

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***Credit Author Statement**

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Laetitia E. Pichevin: Conceptualization, Methodology, Validation, Visualization, Investigation, Writing, Visualization, Funding acquisition, Project administration.

Raja Ganeshram: Conceptualization, Writing - Review & Editing, Funding acquisition, Project administration.

Matthew Dumont: Writing - Review & Editing, Software, Visualization.

***Declaration of Interest Statement**

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: